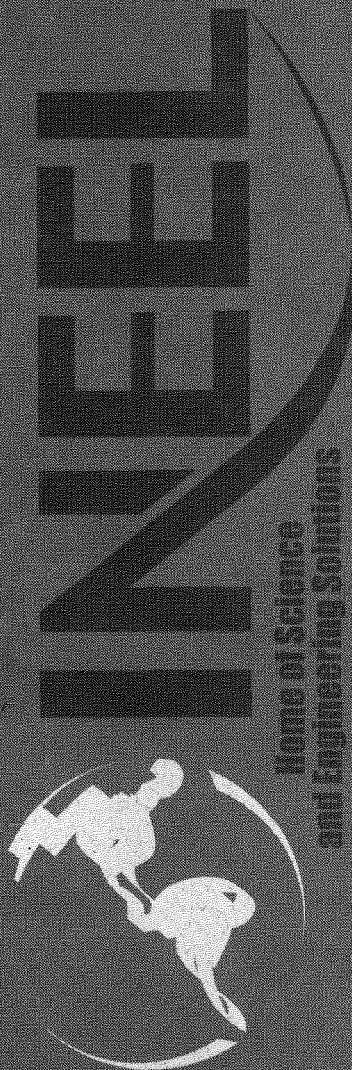


Interim Report for the Plutonium Aquifer Background Study

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*Idaho National Engineering and Environmental Laboratory
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ABSTRACT

Under contract with the Idaho National Engineering and Environmental Laboratory, Los Alamos National Laboratory performed a study to evaluate background plutonium concentrations in the Snake River Plain Aquifer and determine plutonium abundance and isotopic composition and neptunium abundance in groundwater samples collected at the Idaho National Engineering and Environmental Laboratory. Los Alamos National Laboratory Report No. LA-UR-03-2113 was published March 31, 2003, and the body of that report is contained herein.

EXECUTIVE SUMMARY

As part of the “Aquifer Background Study”, Los Alamos National Laboratory (LANL), under contract with the Idaho National Engineering and Environmental laboratory (INEEL) has undertaken a study to determine plutonium abundance and isotopic composition and neptunium abundance in groundwater samples collected at the INEEL. In an earlier phase of this study (Roback, 2002) four samples were analyzed for uranium and plutonium and an additional nine samples were analyzed for uranium. This report summarizes results of plutonium and neptunium analyses on a total of 15 samples using an analytical technique that differs slightly from previous methods. This new technique is designed to provide better sensitivity for plutonium and also provides neptunium-237 concentrations, which were not provided by earlier methods. Four of the samples analyzed for this study were those run in the earlier phase of the project.

Of the 15 samples analyzed only one sample has detectable Pu and ^{237}Np . Plutonium-239 and ^{237}Np abundances in this sample are $1.98\text{E}7$ and $4.4\text{E}8$ atoms for the 733g water sample. The $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio is 0.05, a ratio that is found in weapons-grade plutonium or plutonium generated in nuclear reactors that have operated for only a short time (low burnup). Corresponding activities for these Pu and Np data are approximately 0.6 femtocuries (fCi) $^{(239+240)}\text{Pu}$ and 0.12 femtocuries ^{237}Np . Neither plutonium nor neptunium was detected in the remaining 14 samples at detection limits of approximately $1\text{E}6$ ^{239}Pu and $7\text{E}6$ ^{237}Np atoms. These detection limits correspond to activities of (assuming a $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of 0.05) 0.03 fCi and 0.002 fCi respectively.

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1. INTRODUCTION AND BACKGROUND

To document possible radionuclide migration into the subsurface, INEEL contracted LANL to analyze groundwater samples for plutonium and uranium concentration and isotopic composition by Isotope Dilution-Thermal Ionization Mass Spectrometry (ID-TIMS). An initial set of samples was analyzed for U and Pu concentration and isotopic composition in early 2002 (Roback, 2002). This report summarizes results from a second set of 15 sample analyzed for Pu and ^{237}Np . Some of the samples in the second set were analyzed for U and Pu in the first set. These samples were selected for one or both of the following reasons: 1) samples had positive detections of ^{238}Pu in alpha spectrometric analyses; 2) samples are located in a proximal, down gradient position with respect to the INTEC, RWMC, TRA, or NRF, all possible sources of actinide contaminants. Thus, the samples were selected to maximize the likelihood of identifying actinide contaminants in the aquifer.

2. METHODS

2.1 Sample Collection

Samples were collected from regional aquifer wells with dedicated pumps by INEEL personnel using established sampling protocol. All samples were collected in pre-cleaned I-Chem HDPE bottles to minimize the potential contamination. The samples were acidified in the field with high-purity HNO_3 acid to a $\text{pH} < 2$ and shipped to LANL.

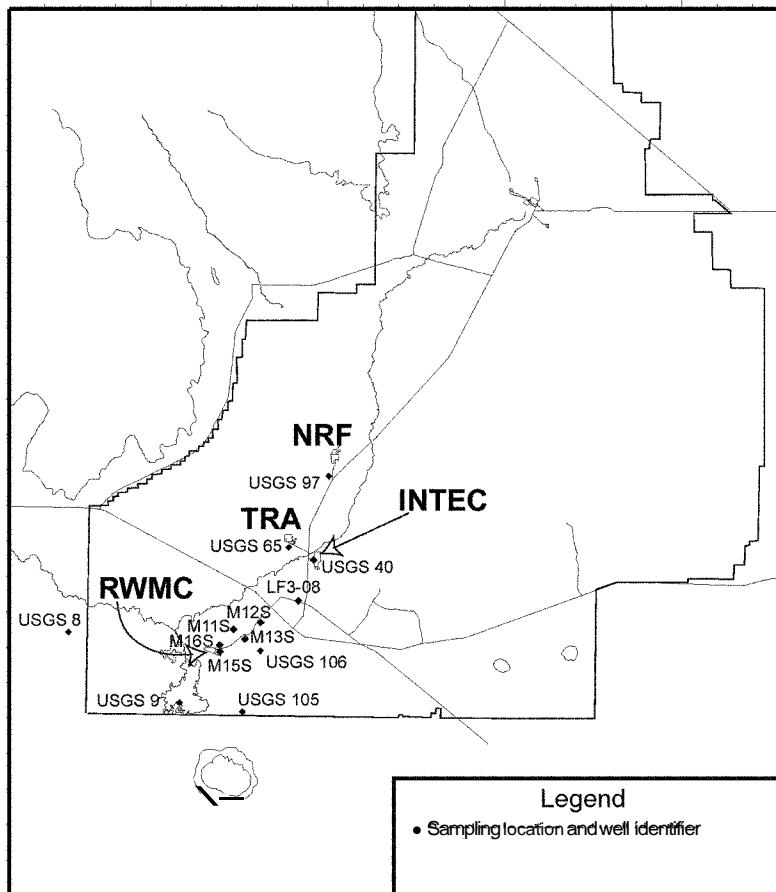


Figure 1. Map of the INEEL showing sample locations.

2.2 Sample Processing and Analysis

All dissolution and chemical separation was performed at the Clean Chemistry and Mass Spectrometry Facility (TA 48, RC 45) at LANL. Ultrapure reagents produced by Seastar™ and Optima™ were used. Groundwater samples were weighed and evaporated in Teflon beakers. To minimize the possibility that the plutonium had sorbed to the sides of the sample bottle, 10 ml of concentrated nitric acid were added to each sample bottle, and the bottle was warmed on a hot plate for 24 hours. To further ensure against the potential loss of plutonium onto the sides of the sample bottles by sorption, the bottles were “washed” by adding approximately 20 ml of concentrated nitric acid to about 100 ml of the remaining sample and placing the bottles, loosely capped on a warm hot plate for 24 hours. This nitric acid + sample wash was added to the samples. The combined solutions were then evaporated to dryness.

The precipitated salts were redissolved in a mixture of concentrated HNO_3 , HF, and perchloric acids and dried. The sample was redissolved in 3M HCl and concentrated HClO_4 ; all samples readily dissolved. The dissolved samples were spiked with ^{244}Pu and ^{236}Np tracers and neodymium carrier and taken to dryness with the perchloric acid to achieve sample-tracer equilibration. Samples were redissolved in 0.5 M HCL in preparation for purification steps.

Plutonium and neptunium were purified using two coprecipitations as neodymium oxalate and ferric hydroxide. The coprecipitations are selective for lanthanides and actinides in the trivalent and tetravalent states and also provide substantial U separation. Precipitates were redissolved in hydrochloric acid. Pu and Np were separated from Fe, Nd and the other lanthanides, and actinides including Am, Cm, and Th by two anion exchange separations (AG1-X4-100-200 mesh resin; column volumes of 2 and 0.1 mL respectively). The coprecipitation and anion exchange separations were each proceeded by steps to adjust the Pu and Np to the IV oxidation state, utilizing either an iron (II)-hydroxylamine reducing agent or hydrochloric acid drydown. The purified samples were sorbed onto single resin beads (AG1-X4-100-200). The resin beads were then loaded onto rhenium filaments for thermal ionization mass spectrometric analysis. Plutonium analyses were performed on a VG Sector 54 equipped with a Wide-Angle Retarding Potential (WARP) filter. The single resin beads, onto which the Pu and Np had been sorbed, were loaded onto Re filaments. For all samples, data were collected in ion counting mode. Plutonium and neptunium ratios were corrected for instrument fractionation, background, and spike contribution.

2.3 Quality Control Samples

Samples were processed in three groups of five samples with one blank processed per group. The blanks were processed side by side with the samples and were treated in the same fashion as the samples. Additional samples that may be also considered as quality control samples include duplicate analyses of samples USGS 8 and USGS 9 and a field blank collected at USGS 105. Mass spectrometry of the three blanks produced very low count rates, and therefore very high uncertainties. The few counts observed for the blanks are from a combination of interferences from isobaric compounds, electronic noise inherent in the mass spectrometer, and actual Pu and Np ions. Accurately distinguishing among these is not possible. Nonetheless, the blanks allow a realistic assessment of the total Pu and Np signal background and therefore of our detection limits for these groups of samples. The average ^{239}Pu and ^{237}Np background for the three blanks is 4.4E5 and 2.6E5 respectively. These values were subtracted from the sample values to arrive at the final reported values for the samples.

Two samples, USGS 8 and USGS 9, were processed in duplicate. These samples were selected as duplicates because alpha spectrometry measurements performed as part of the INEEL EM program showed detections of $^{(239+240)}\text{Pu}$ at the 95% confidence level. A single sample, USGS 105, is a field blank, which consisted of ultrapure water that was brought to the field and transferred to a sample bottle during collection of the actual sample. The purpose of the field blank is to assess if wind blown dust may have contaminated the samples. Neither Pu nor Np was detected in the QA samples.

3. RESULTS

Table 1. Summary of Pu and Np results.

Sample Number	Sample ID	Sample Wt (g)	²³⁹ Pu atoms in sample	Error %	²⁴⁰ Pu/ ²³⁹ Pu	Error %	²⁴¹ Pu/ ²³⁹ Pu	Error %	²³⁷ Np atoms in sample	Error %
1	USGS 8	999.5	2.29E+04	100					5.7E+06	100
2	USGS 9	812.2	-1.09E+04	>100					3.1E+06	>100
3	USGS 106	1014.4	-7.11E+04	>100					1.8E+06	>100
4	M11S	1005.4	1.09E+06	59					4.3E+06	>100
5	M15S (formerly 09)	1009.9	-6.95E+03	>100					6.7E+06	116
6	Process Blank A		2.46E+05	>100					3.6E+06	>100
7	USGS 40	733.3	1.98E+07	5.0	0.05	16	0.005	71	4.4E+08	3.0
8	USGS 65	788.0	-1.42E+05	>100					4.8E+05	>100
9	USGS 97	986.0	5.18E+04	>100					9.3E+05	>100
10	M13S	980.0	-1.06E+05	>100					1.4E+06	>100
11	USGS 8 duplicate	1005.6	2.28E+05	>100					-1.7E+06	>100
12	Process Blank B		7.88E+05	>100					-4.0E+06	>100
13	USGS105 Field Blank	1005.6	-4.31E+05	>100					2.3E+06	>100
14	LF3-08	768.5	-5.38E+05	>100					6.3E+06	123
15	M12S	1001.8	1.23E+06	52					4.7E+06	>100
16	M16S (formerly 010)	994.3	-5.93E+05	>100					9.7E+05	>100
17	USGS 9 duplicate	1003.5	4.61E+04	>100					4.2E+06	>100
18	Process Blank C		2.81E+05	>100					1.2E+06	>100

Sample data are corrected for process blank of 4.4E5 ²³⁹Pu, 1.8E5 ²⁴⁰Pu and 2.6E5 ²³⁷Np atoms.

Errors are 2-sigma

Plutonium-239 and ²³⁷Np are expected to be the most abundant isotopes of Pu and Np in these samples, and therefore the most readily detectable by mass spectrometry. Plutonium-239 and ²³⁷Np were detected in only one sample, **USGS 40**. The blank-corrected ²³⁹Pu and ²³⁷Np concentrations are $1.98E7 \pm 5\%$ (all errors are reported at the 2-sigma level) and $4.4E8 \pm 3\%$ atoms respectively. The ²⁴⁰Pu/²³⁹Pu ratio is $0.05 \pm 16\%$ and the ²⁴¹Pu/²³⁹Pu ratio is $0.005 \pm 71\%$. The low ²⁴⁰Pu/²³⁹Pu atomic ratios measured for this sample are consistent with either weapons-type plutonium or Plutonium derived from low burnup nuclear fuels. The data are not consistent with plutonium that originated from atmospheric fallout, which was determined by Beasley et al. (1998) to be approximately 0.17 for the INEEL.

3.1 Discussion of Detection Limits

Neither Pu nor Np is considered to be present in the other samples above detection limits for Pu and Np. Assessment of detection limits are based on analysis of the QA samples run as part of this study as well as the longer-term history of the laboratory. The “detection limit” as applied here reflects the sensitivity of the analytical method (isotope dilution-thermal ionization mass spectrometry), that is, the number of atoms that can be counted per samples, and our confidence in evaluating the source of these counts. As mentioned above, ions counted by a mass spectrometer may have different sources including: electronic noise, isobaric molecules (e.g. ²³⁸UH⁺ at mass 239), blank, and actual sample. As total counts rates per sample decrease the relative contribution of the first three of these sources increases. At the detection limit, the relative contributions of electronic noise, isobaric molecules, blank, and actual sample cannot be distinguished.

The mean value of ²³⁹Pu atoms in three laboratory blanks is 4.4E5 atoms. Individual uncertainties of these are high (>100%) due to the extremely low count rates. Furthermore, the standard deviation among the three blanks is also high. Data for all samples considered below detection and the laboratory blanks are plotted in Figure 2. It is apparent from the plot that most of the sample data, including the field blank and duplicates are indistinguishable from the blanks. Two samples, M11S and M12S, number 4 and 15 on Figure 2; however, have higher ²³⁹Pu abundances than the blanks and the rest of the samples. Despite this suggestion of detectable ²³⁹Pu, these analyses are considered to be below the detection limits

for the following reasons: 1) the ^{240}Pu contents for these two samples are negative, 2) they do not show detectable Np, which is well above detection in sample **USGS 40**, and 3) ^{239}Pu blanks have been measured for other projects using the same laboratory and a similar procedure to that in this study that are comparable to values measured for M11 and M12. This evidence suggests that the ^{239}Pu measured for M11 and M12 does not represent true detection. These two samples should; however, be considered as high priority for reanalysis in future studies.

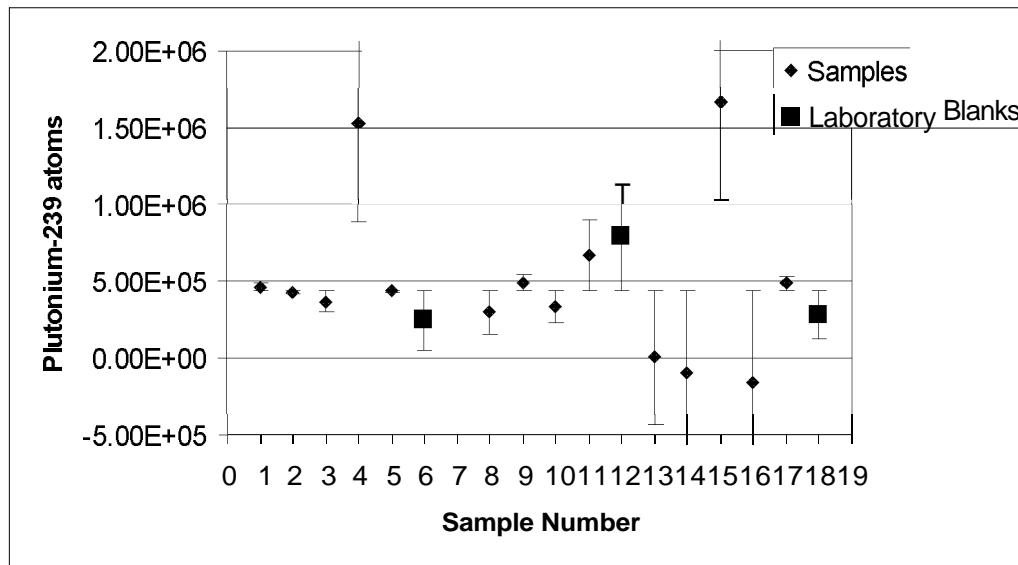


Figure 2. Plot of ^{239}Pu atoms for all samples and laboratory blank with 2-sigma uncertainties. Data for sample 7 plot well above at this scale

4. REFERENCES

Beasley, T. M., J. M. Kelley, L. A. Bond, William Rivera, Jr., M. J. Liszewski, and K. A. Orlandini, 1998, *Heavy Element Radionuclides (Pu, Np, U) and ^{137}Cs in Soils Collected from the Idaho National Engineering and Environmental Laboratory and Other Sites in Idaho, Montana, and Wyoming*, *Environmental Measurements Laboratory Report*, EML-599, Los Alamos National Laboratory.